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Relationships between Polyurethane Elastomer Structure and Ageing Properties: Part 1: Degree of Crosslinking

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Relationships between Polyurethane Elastomer Structure and Ageing Properties: Part 1: Degree of Crosslinking

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SUMMARY

The effects of crosslink density on the ageing properties of polyurethane elastomers have been studied using a series of typical polyester and polyether urethanes of M_c values (average molecular weight between crosslinks) between 2 500 and infinity. While the unaged polyester urethane elastomers showed the highest strengths, the polyether urethane elastomers showed superior hydrolytic stability.

An optimum balance between mechanical properties and the resistance to hydrolysis and standard test fluid appeared to be achieved with a relatively high degree of crosslinking ie M_c values of less than 5 000.

Unlike the polyether elastomers, unaged polyester elastomers yielded higher modulus and hardness as the crosslink density diminished, ie M_c values > 12 000, suggesting that intermolecular forces as well as crosslink density are important factors governing the properties of polyesters.

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Reference: WAC/207/021

1 INTRODUCTION

The properties of polyurethane elastomers have been discussed recently,[1] suffice to mention here that the main disadvantages of polyurethane elastomers which make then unattractive for many Service and industrial applications are that polyester urethanes are sensitive to hydrolysis and solvents, while polyether urethanes are in addition susceptible to photoxidation.

Improvements to the hydrolytic stability of polyurethane elastomers have been reported recently.[1] This was achieved by replacing conventional polyfunctional polyether and polyester backbone diols with hydroxyl-terminated polybutadienes. Unfortunately the resistance of these materials to petrol was not very satisfactory and their mechanical properties left room for improvement.

In view of the fact that many commercial manufacturers are reluctant to divulge the formulations of their materials, it was considered desirable to establish the effects of chemical structure on the ageing properties of polyurethane elastomers of known chemical composition prepared under laboratory conditions.

Although there is considerable information in the literature, much of it from common sources, on relationships between urethane polymer structure and polyurethane elastomer properties,[2(a),3-6,7(a),8-10] these have been related mainly to initial properties, for example, mechanical properties, glass transition temperature (T_g) and swelling.[11-15] The effects of ageing, for example, outdoor exposure,[16] hydrolysis,[17-21] sorption diffusion,[22] elevated temperatures[23-25] and photoxidation[26-28] have been studied with selected or commercial polymers; however, there appears to be little or no information in the open literature of any systematic studies of the relationships between structure of polyurethane elastomers and their ageing properties. The main objectives of the present investivation, therefore, are to study the effects of changes in structure of polyurethane elastomers in relation to their ageing characteristics and to attempt to formulate elastomers which achieve an optimum balance between initial mechanical properties and resistance to ageing.

The first report in the present series considers the effects of the degree of crosslinking on the ageing properties of both a typical polyester and a typical polyether urethane elastomer formulated to give six different M_c values (average molecular weight between crosslinks). Crosslinking in polyurethane elastomers normally occurs by the reaction of excess isocyanate either with urethane groups to form allophanate linkages, or with urea groups to form biuret linkages. The elastomers described in the present report, however, should contain predominantly urethane crosslinks. This was achieved by reacting equivalent amounts of active hydrogen backbone diol components with a di-isocyanate and known molar quantities of trifunctional triol crosslinking agent and difunctional diol chain extender. The degree of crosslinking was therefore a function of the ratio of triol to diol used.

2 MATERIALS AND METHODS OF PREPARATION

All the elastomers were prepared via toluene di-isocyanate (TDI) prepolymers using either a laboratory prepared polyester, poly(1,4-butylene)adipate (average molecular weight 2 050, hydroxyl number 54.7, acid number 0.14, percentage water 0.01), or a commercially supplied polyether, polyoxybutylene glycol ('Polymeg' ex-Quaker Oats Co., average molecular weight 2 000, hydroxyl number 56.0, acid number 0.01, percentage water 0.01); these materials were selected because of their similar chemical structures, as well as being fairly typical of polyols used commercially. An attempt to produce a series of elastomers (S1 - S6) of M_c values 2 500 to ∞ using a polydiethylene adipate polyester was unsuccessful yielding thermoplastic non-elastic materials at M_c values above 4 000.

The polyester or polyether 1.0 mole equivalent was reacted with 3.0 moles equivalent of toluene di-isocyanate, TDI (Hylene T.M. ex-Du Pont UK), a mixture of 80 per cent 2,4 and 20 per cent 2,6 isomers. The prepolymers were reacted with 0.1 to 2.0 moles of either trimethylol propane or 1,4-butane diol, or both, in order to give the required molecular weight between crosslinks as follows.

$$M_c = \frac{P + I + C + L}{T}$$

where M_c = molecular weight between crosslinks

P = g/mol equivalents of polyester or polyether

I = " " " di-isocyanate

C = " " " chain extender (diol)

L = " " " crosslinker (triol)

T = molar amount of trifunctional reactant.

Brief details of the formulations and identification numbers of the elastomers are recorded below.

	S77 Moles	S88 Moles	S99 Moles	S100 Moles	S111 Moles	S12 Moles
Polyoxybutylene glycol	1.0	1.0	1.0	1.0	1.0	1.0
TDI	3.0	3.0	3.0	3.0	3.0	3.0
1,4-Butane diol	2.0	1.85	1.7	1.5	1.0	0.5
Trimethylol propane	-	0.1	0.2	0.35	0.66	1.0
Theoretical M_c value	∞	26 700	13 300	8 000	4 000	2 675

	S13 Moles	S14 Mole	S15 Moles	S16 Moles	S17 Moles	S18 Moles
Poly(1,4-butylene) adipate	1.0	1.0	1.0	1.0	1.0	1.0
TDI	3.0	3.0	3.0	3.0	3.0	3.0
1,4-Butane diol	2.0	1.85	1.7	1.5	1.0	0.5
Trimethylol propane	-	0.1	0.2	0.33	0.66	1.0
Theoretical M_c value	∞	26 500	13 750	8 250	5 500	2 750

Two controls were assessed for comparison, these were S12A, polyoxybutylene glycol and S18A, poly(1,4-butylene)adipate, respectively based on polyol 1.0 mole, TDI 2.1 moles and trimethylol propane 0.66 mole and should contain both urethane and allophanate crosslinks. The diols and triols were analytical quality and re-distilled, no catalyst or other additives were used. The reaction products were sealed under nitrogen, in dried nitrogen flushed container. The methods of preparation were similar to those described in Ref.1. Summarised details are recorded in Appendix A.

The isocyanate content of the prepolymers was determined using the method described in Ref.3.

The reaction products were poured into PTFE coated steel trays and cured in an oven for 16 h at 90°C to produce sheets 220 × 150 mm, 2.5 mm thick.

3 EXPERIMENTAL

British Standard type E dumb-bell test pieces (four per test) were cut from the cast sheets and the width and thickness measured before exposure to the test conditions. Dumb-bells, in sets of four, were suspended in loosely stoppered glass tubes and exposed to some of the following environments for twenty-eight days.

Controls	Conditioned in air at 20°C
Hot/dry	Suspended in air at 80°C
Hot/wet	Immersed in boiled out distilled water at 80°C
*Standard Test Fluid	Immersed in Standard Test Fluid at 65°C

The charged tubes were placed in circulating air ovens in which the temperatures did not vary by more than ±0.5°C from the test temperature. After twenty-eight days' exposure the tubes and contents were removed from the oven and conditioned at room temperature for 24 hours before testing. After the conditioning period, the groups of four specimens were removed from the tubes, dried from a superficial liquid, and tested for hardness, moduli, extension at break and tensile-strength as quickly as possible. Hardness was measured using a micro-indentometer,

*Standard Test Fluid (STF) consists of a 70/30 v/v mixture of iso-octane and toluene, and is intended to represent a standard "medium to high aromatics" content petrol. [29]

and the tensile properties were measured by British Standard Methods[30,31] on a Hounsfield Tensometer. Unaged control specimens cut from the materials were tested by the same methods, and the results used as "unaged" reference points. The glass transition temperatures (T_g) of the elastomers were recorded by a Perkin-Elmer Differential Scanning Calorimeter at a rate of heating of 16°C/min with the specimens sealed in a standard aluminium pan.

4 RESULTS AND DISCUSSION

The visual appearances of the elastomers before and after ageing are recorded in Table 1.

The T_g of unaged elastomers and the mechanical properties of the elastomers before and after ageing for twenty-eight days are recorded in Table 2.

The percentage changes in the original mechanical properties of the elastomers after ageing are recorded in Table 3.

4.1 Visual Appearance

Judged solely by visual and empirical assessments which are summarised in Table 1, the general condition of the polyurethane elastomers after ageing is described below.

4.1.1 Initial

Unaged polyether urethane elastomers of M_c values 26 700 to ∞ showed two phases, one opaque the other opalescent; on the other hand, polyester urethane elastomers at these two M_c values were completely opaque. The two phases described above were observed with polyester urethanes at M_c values of 5 500 - 13 750, but polyester urethane elastomers of M_c 2750 were clear. The remaining polyether urethanes of M_c values 13 300 and below were slightly opalescent, including the polyether urethane control: the polyester urethane control however was opaque.

According to Buist[2] the significance of opalescence or opacity in urethane elastomers is obscure and may be associated with crystallisation of polyurethane segments, or, alternatively, indicate a phase separation which may be either crystalline or amorphous. Polyesters S14 - 16 (M_c 8 000 - 26 000) however were definitely crystalline.

4.1.2 Dry Air

After twenty-eight days in dry air at 80°C, all the polyester and polyether urethane elastomers, apart from a polyether elastomer of M_c value 26 700 which was very soft, appeared to be in reasonably good condition. Polyether elastomers at M_c values above 8 000 however showed some discolouration. The polyester elastomers were rather more brittle than the polyether elastomers.

4.1.3 Immersion in water

After twenty-eight days in water at 80°C there was no doubt that certain of the polyether based urethane elastomers showed superior hydrolytic stability to the polyester based elastomers.

All the polyester urethanes of M_c values 2 750 to ∞ showed catastrophic or severe breakdown, eventually disintegrating into brown viscous liquids. Similarly, all the polyether urethanes of M_c values exceeding 13 300 showed similar failures. However, at M_c values of below 13 300 and especially between M_c 2 675 and 8 000, the polyether elastomers, apart from some discolouration, were in good condition.

4.1.4 Immersion in STF (Petrol)

After twenty-eight days' immersion in STF at 65°C, all the polyether elastomers of M_c values exceeding 13 300 showed failures due to severe swelling. All the polyester elastomers of similar M_c values also showed severe failures and disintegrated into a white opaque plastic mass. Both polyester and polyether urethane elastomers of M_c values 2 675 to 8 250 appeared to be little affected by immersion in STF. Similarly, both the polyester and polyether controls were also in good condition after immersion in STF.

4.2 Mechanical Properties

The initial mechanical properties of the elastomers and the changes induced by ageing are given in Tables 2 and 3 and are shown graphically in Figs 1 - 4. A more detailed discussion is given below.

4.2.1 Initial Properties

Polyester and polyether elastomers show fundamental differences in tensile behaviour as the crosslink density changes. The polyether elastomers show a considerable decrease in tensile strength as M_c increases whereas the polyesters although showing a sharp fall in tensile strength between M_c values of 5 000 and 15 000 subsequently show a slow rise as M_c increases further. Literature values for a polyethylene adipate urethane are given for comparison (Fig 1).

The 100 per cent modulus and extension at break figures sharply distinguish between the polyester and polyether elastomers. At M_c values of approximately 5 000 the two materials show similar moduli and extensions at break. However, the polyesters are characterised by a rapid increase in modulus associated with little change in extension as M_c increases whereas polyethers show a rapid fall of modulus and an increase in extension at break to well over 1 000 per cent as M_c increases.

The greater strengths of polyester urethanes is attributable to higher intermolecular forces (hydrogen bonding) and increased crystallinity in these materials as M_c increases. The molar cohesive energy of the - COO - (ester) group is widely reported as 12.1 kJ/mol (2.9 kcal/mole) compared to 4.2 kJ/mol (1.0 kcal/mole) for the - O - (ether) group.

The effects of crosslinking on the stress-strain properties of normal elastomers at temperatures above T_g is well established.[32] Extension at break deceases as crosslinking increases (M_c decreases); the tensile strength first increases and then decreases. However in polyurethanes the introduction of crosslinking changes to some extent the basic chemical structure of the material and it is not so easy to establish how crosslinking contributes to the observed changes in mechanical properties. Furthermore in a material liable to crystallisation,

crosslinking may prevent this occurring except under stress thus producing a another variable. Polyether urethanes follow the general predicted pattern for amorphous materials whilst the behaviour of polyesters can be explained on the basis that increasing the crosslink density results in a reduced tendency for crystallisation shown as a fall in modulus at low M_c values.

4.2.2 Ageing in Dry Air

After ageing in dry air at 80°C polyether elastomers show relatively small changes at M_c values below 12 000. The polyester elastomers all show some changes becoming stronger on ageing at the higher crosslink densities. S17 shows anomalous behaviour which will be investigated later.

4.2.3 Immersion in Water

At M_c values below 4 000 polyether urethanes showed reasonable ageing behaviour in water whereas none of the polyester urethanes retained a measurable mechanical property at any M_c value. This result demonstrated that it must be the ester link which is responsible for the poor hydrolytic stability since both series of elastomers should contain similar predominantly urethane linkages. The polyether urethane control which contained both urethane and allophanate linkages was no more susceptible to degradation than the similar material containing predominantly urethane linkages.

Possible products of hydrolysis are shown below.

Ester	R.CO.O.R'	$\xrightarrow{H_2O}$	R.COOH + R'OH
Ether	R.O.R'	→	R.OH + R'OH
Urethane	R.NH.CO.O.R'	→	$R.NH_2$ + R'OH + CO_2
Allophanate	R.NH.CO.NR".CO.OR'	→	R.NH.CO.NHR" + CO + R'OH

It is hoped that further work will prove whether scission in polyester occurs at the ester or urethane link.

4.2.4 Immersion in STF

With both polyester and polyether urethane elastomers a high degree of crosslinking (low M_c values) is necessary to achieve resistance to swelling by petrol. With the type of polyester elastomers examined M_c values of less than 2 500 are necessary. For the polyether elastomers M_c values of less than 7 500 especially between 4 000 and 6 000, gave the most satisfactory retention of mechanical properties after ageing. The polyether elastomer of M_c 2 675, however, showed surprisingly poor resistance to STF considering it was the most highly crosslinked polyether.

4.3 Glass Transition Temperature, T_g

The recorded glass transition temperatures for the two series of polyurethanes are reported in Table 2. The values fall into two groups, the polyethers with the exception of S12 and S12A at approximately -40°C whereas the polyesters fall

between -10 and -23°C. The polyethers therefore have better low temperature properties than the polyesters. Measurements were very difficult with S13 - 15 due to recrystallisation.

There was no systematic trend of T_g with degree of crosslinking whereas in general T_g increases with increasing crosslink density according to an approximate relation $T - T_g = \frac{3.9 \times 10^4}{M_c}$ where $(T - T_g)$ is the increase in T_g as the molecular weight between crosslinks decreases from ∞ to M_c.

Similar studies reported in the literature have also shown T_g of certain polyurethane series to be independent of structure.[7(b), 18]

A possible explanation of this effect is that the crosslinking of this type of polyurethane can be regarded not just as a simple linking of chains but as a copolymerisation of triol units into the backbone. Therefore the shift in T_g is made up of (a) the effect due to increasing the crosslink density which raises T_g, and (b) the effect of copolymer units which may raise or lower T_g.

An alternative explanation suggests that polyurethanes exist in a similar physical form to thermoelastomers and have domains of urethane rich areas in a continuum of non-urethane phase, the T_g being determined by the properties of the continuum.[2(b)]

5 CONCLUSIONS

Many of the polyurethane elastomers assessed in the present investigation showed catastrophic breakdown and could readily be rejected on visual examination. The properties of the polyether urethanes based on poly(oxy-1,4-butylene)glycol were highly dependent on crosslink density. With polyester urethanes, based on poly(1,4-butylene)adipate, hydrogen bonding and crystallinity were important additional factors. The glass transition temperature of both series was little affected by changes in crosslink density.

The polyether urethane elastomers containing predominantly urethane linkages, behave, with respect to hardness and modulus - particular, as non-crystalline polymers which possess a relatively low degree of effective intermolecular forces. As the crosslink density decreases (increase in M_c value), the polymer changes from a hard rubbery highly crosslinked structure with reasonable resistance to swelling by STF and hydrolysis by hot water, to a material with less resistance to water and STF and finally, with little effective crosslinking, to a linear thermoplastic polymer which is severely swollen by STF and disintegrated by hot water. The optimum balance between initial mechanical properties and resistance to dry air, hot water and petrol (STF) is achieved by fairly highly crosslinked elastomers with M_c values of between 2 750 and 5 000.

The polyester urethane elastomers based on poly(1,4-butylene)adipate ester (average molecular weight 2 000) TDI polymers containing predominantly urethane linkages showed an increase in modulus and hardness with decreasing crosslinking (increasing M_c values) and were thus fairly typical of polymers with a fairly high degree of intermolecular attraction. Although none of the polyester urethane elastomers were hydrolytically stable their resistance to swelling by

STF improved with increasing crosslinking. With this type of elastomer the optimum balance between initial mechanical properties and resistance to ageing was again achieved at M_c values of less than 4 000. Where polyester urethanes based on polybutylene adipate/TDI possessing a high modulus are required, large M_c values of 12 000 are needed.

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PREPARATION OF ELASTOMERS

PREPOLYMERS

	PPS/4		PPS/5	
	moles	g	moles	g
Polyoxybutylene glycol (Av. mol. wt. 1 976) Polymeg ex-Quaker Oats Ltd	1.0	985	-	-
Poly(1,4-butylene)adipate (Av. mol. wt. 2 050) Laboratory prepared			1.0	1 025
Toluene di-isocyanate (Mol wt. 174) Ex-Du Pont (UK)	3.0	266	3.0	266

Method

To a two-litre reaction flask, fitted with a detachable five-necked cover equipped with heating-mantle, stirrer, thermometer, vacuum and nitrogen inlet was added the TDI. The temperature was raised to 80°C over 30 minutes under nitrogen. The polyol was added over $\frac{1}{2}$ - $\frac{3}{4}$ h with continuous stirring. The reaction continued for 3 h at 80 - 85°C under nitrogen. The reaction products were placed in oven-dried nitrogen flushed glass containers and sealed under nitrogen.

ELASTOMERS

The elastomers S7 - S18 were prepared in 500 ml three-necked glass flasks equipped with heating mantle, stirrer, thermometer and nitrogen inlet. 1.0 mole equivalent of prepolymer PPS/4 or PPS/5 was heated to 80°C and degassed under vacuum 5 mmHg for 30 minutes. 0.1 to 2.0 moles equivalent of either trimethylol propane, 1-4 butane diol or a mixture of both was added and stirred for five minutes. The product was degassed for 10 minutes under vacuum 1 mmHg and the reaction products cast in preheated PTFE coated steel trays and cured for 16 h at 90°C.

A

GENERAL CONDITION AND AP

Type of Elastomer	Code Number	M_c	Unaged	
	S7	∞	Very pale lemon, $\frac{1}{3}$ opaque, $\frac{2}{3}$ opalescent, soft, relatively inflexible	Ca
POLYETHER	S8	26 700	Very pale lemon, $\frac{1}{2}$ opaque, $\frac{1}{2}$ opalescent, soft, inflexible	Ca
	S9	13 300	Very pale lemon, opalescent, soft and weak	Ca
	S10	8 000	Very pale lemon, opalescent, flexible	Br in
	S11	4 000	Very pale lemon, opalescent, tough and flexible	Br
	S12	2 675	Very pale lemon, opalescent, tough and flexible	Yel int
	S12A Control		Very pale lemon, opalescent, tough and flexible	Yel cor
POLYESTER	S13	∞	White opaque, tough, slightly inflexible	Cat
	S14	26 500	Pale yellow opaque, tough, slightly inflexible	Cat
	S15	13 750	$\frac{1}{4}$ almost clear, $\frac{3}{4}$ opaque pale yellow, tough, slightly inflexible	Cat
	S16	8 250	$\frac{1}{3}$ almost clear, $\frac{2}{3}$ opaque pale yellow, tough, flexible	Cat
	S17	5 500	$\frac{1}{3}$ almost clear, $\frac{2}{3}$ opaque pale yellow, tough, flexible	Sev liq
	S18	2 750	Clear, tough, flexible	Sev
	S18A Control		White, slightly opaque, tough, flexible	Sev

B

TABLE 1

APPEARANCE OF POLYURETHANE ELASTOMERS

Immersed in water for 28 days at 80°C	Exposed in dry air for 28 days at 80°C	Immersed in STF for 28 days at 65°C
Catastrophic failure, brown liquid	Yellow, fairly good condition	Pale yellow, soft but intact
Catastrophic failure, brown liquid	Amber, soft	Catastrophic failure, yellow liquid
Catastrophic failure, brown liquid	Amber, slightly harder	Pale yellow, intact but sticky
Brown, fairly good condition, intact but soft	Amber, intact, good condition	Pale lemon, intact, good condition
Brown, good condition, intact	Pale yellow, intact, good condition	Pale lemon, intact, good condition
Yellow brown, good condition, intact	Pale yellow, intact, good condition	Pale lemon, intact, good condition
Yellow brown, intact, good condition	Pale yellow, intact, good condition	Pale lemon, intact, good condition
Catastrophic failure, brown liquid	Lemon opaque, slightly inflexible	Catastrophic failure, white opaque plastic mass
Catastrophic failure, brown liquid	Lemon opaque, rather brittle	Catastrophic failure, white opaque plastic mass
Catastrophic failure, brown liquid	Pale lemon translucent, slightly brittle	White opaque, slight disintegration
Catastrophic failure, brown liquid	Very pale lemon, translucent, slightly brittle	White opaque, intact, brittle
Severe failure, pale amber brown liquid	Pale lemon, clear, slightly brittle	Pale lemon, slightly opaque, intact, good condition
Severe failure, brown liquid	Clean, good condition	Pale lemon, clear, intact, good condition
Severe failure, dark brown liquid	Lemon, clear, good condition	Pale lemon, clear, intact, good condition

A

TABLE

Type	Code Number	M_c	Modulus at 100 per cent extension (MN/m^2)			
			Unaged	80°C (dry)	80°C (wet)	65°C (STF)
POLYETHER	S7	∞	0.8	0.1	F	R
	S8	26 700	R	R	F	F
	S9	13 300	R	R	F	F
	S10	8 000	0.3	0.1	R	0.4
	S11	4 000	1.0	0.6	R	0.1
	S12	2 675	2.9	0.8	0.5	-
	S12A	CONTROL	1.2	0.7	0.5	-
POLYESTER	S13	∞	11.0	-	F	F
	S14	26 500	10.1	0.7	F	F
	S15	13 750	8.0	2.2	F	F
	S16	8 250	4.5	0.3	F	1.3
	S17	5 500	3.3	0.6	F	0.4
	S18	2 750	0.9	0.9	F	0.9
	S18A	CONTROL	2.0	0.7	F	1.0

6.9 MN/m^2 = 1 000 p

F = impossi

R = value t

TABLE 2 (contd.)

Modulus at 100 per cent extension (MN/m^2)				Modulus at 200 per cent extension (MN/m^2)				Modulus at 300 per cent extension (MN/m^2)			
ged	80°C (dry)	80°C (wet)	65°C (STF)	Unaged	80°C (dry)	80°C (wet)	65°C (STF)	Unaged	80°C (dry)	80°C (wet)	65°C (STF)
.8	0.1	F	R	R	0.4	F	R	R	0.5	F	R
	R	F	F	R	R	F	F	R	R	F	F
	R	F	F	R	R	F	F	R	R	F	F
.3	0.1	R	0.4	0.5	0.4	R	0.6	0.7	0.6	R	1.2
.0	0.6	R	[illegible]	1.9	1.1	0.3	0.2	3.3	1.9	0.6	-
.9	0.8	0.5	-	5.8	2.3	1.3	-	-	-	2.6	-
.2	0.7	0.5	-	2.5	1.4	1.2	-	-	-	2.6	-
.0	-	F	F	11.0	-	F	F	14.2	-	F	F
.1	0.7	F	F	12.0	7.3	F	F	R	R	F	F
.0	2.2	F	F	8.0	2.8	F	F	8.0	3.8	F	F
.5	0.3	F	1.3	5.1	1.0	F	3.1	5.8	1.3	F	3.5
.3	0.6	F	0.4	3.8	1.0	F	0.7	4.9	1.3	F	1.3
.9	0.9	F	0.9	1.7	1.7	F	2.8	5.7	5.8	F	-
.0	0.7	F	1.0	2.6	1.3	F	-	6.3	4.7	F	-

6.9 MN/m^2 = 1 000 psi

F = impossible to test due to swelling or disintegration

R = value too low to be recorded or not recorded

TABLE 2

[illegible] AND T_g OF POLYURETHANE [illegible]

Type	Code Number	M_c	Tensile strength (MN/m^2)				Extension at br[illegible]	
			Unaged	80°C (dry)	80°C (wet)	65°C (STF)	Unaged	80°C (dry)
POLYETHER	S7	[illegible]	[illegible]	5.2	F	1.0	R	600
	S8	26 700	R	R	F	F	1 380	1 880
	S9	13 300	3.4	2.1	F	F	1 095	930
	S10	8 000	8.1	8.5	2.2	5.0	595	575
	S11	4 000	10.2	17.3	8.0	3.4	415	475
	S12	2 675	4.1	4.0	2.4	0.8	220	210
	S12A	CONTROL	3.0	1.9	5.7	0.7	225	255
POLYESTER	S13	[illegible]	12.8	8.3	F	F	365	20
	S14	26 500	11.4	7.3	F	F	175	360
	S15	13 750	11.3	19.2	F	F	445	535
	S16	8 250	15.8	17.1	F	7.5	450	450
	S17	5 500	23.7	13.3	F	5.2	460	490
	S18	2 750	20.9	30.7	F	34.5	355	385
	S18A	CONTROL	20.7	14.9	F	1.6	370	360

6.9 MN/m^2 = 1 000 psi

F = impossible to test due eithe[illegible]

R = value too low to be recorded

B

ABLE 2

ANE ELASTOMERS BEFORE AND AFTER AGEING 28 DAYS

on at break (per cent)			Hardness (BS°)				T_g (°C)
80°C (dry)	80°C (wet)	65°C (STF)	Unaged	80°C (dry)	80°C (wet)	65°C (STF)	
600	F	330	66	58	F	R	-39
1.880	F	F	R	R	F	F	-39
930	F	F	33	R	F	F	-43
575	745	500	50	40	R	R	-38
475	565	245	66	64	42	56	-40
210	295	50	72	65	61	66	-54
255	440	65	71	68	49	64	-61
20	F	F	98	97	F	F	Not observed
360	F	F	98	98	F	F	" "
585	F	F	98	96	F	F	" "
450	F	350	85	63	F	R	-18
490	F	415	82	32	F	R	-11
385	F	230	67	67	F	67	-12
360	F	155	76	67	F	64	-23

due either to swelling or disintegration

recorded or not recorded

A

TABLE 3

PERCENTAGE CHANGES IN MECHANICAL PROPERTI

Type	Code Number	M_c	Tensile Strength			
			80°C (dry)	80°C (wet)	65°C (STF)	80°C (
POLYETHER	S7	∞	+827	F	+11	R
	S8	26 700	R	F	F	+ 36
	S9	13 300	- 38	F	F	- 15
	S10	8 000	0	- 74	-38	- 3
	S11	4 000	+ 72	- 22	-67	+ 15
	S12	2 675	- 5	- 42	-81	- 5
	S12A	CONTROL	- 37	+ 90	-77	+ 13
POLYESTER	S13	∞	- 35	F	F	- 95
	S14	26 500	- 36	F	F	+106
	S15	13 750	+ 70	F	F	+ 31
	S16	8 250	+ 8	F	-53	0
	S17	5 500	- 44	F	-78	+ 7
	S18	2 750	+ 47	F	+65	+ 9
	S18A	CONTROL	- 28	F	-92	+ 3

F = impossible to tes due either

R = value too low to be recorded

B

TABLE 3

ICAL PROPERTIES OF POLYURETHANES AFTER AGEING 28 DAYS

	Extension at Break			Hardness		
(STF)	80°C (dry)	80°C (wet)	65°C (STF)	80°C (dry)	80°C (wet)	65°C (STF)
	R	R	R	-12	F	R
	+ 36	F	F	R	F	F
	- 15	F	F	R	F	F
	- 3	+25	-16	-20	R	R
	+ 15	+36	-41	- 3	-33	-15
	- 5	+34	-77	-10	-15	- 8
	+ 13	+96	-71	- 4	-31	-10
	- 95	F	F	0	F	F
	+106	F	F	0	F	F
	+ 31	F	F	0	F	F
	0	F	-22	-26	F	R
	+ 7	F	-10	-61	F	R
	+ 9	F	-35	0	F	C
	+ 3	F	-58	-12	F	-16

test due either to swelling or disintegration

to be recorded or not recorded

TABLE

Type	Code Number	M_c	Modulus at 100 per cent Extension			Mo
			80°C (dry)	80°C (wet)	65°C (STF)	80°
POLYETHER	S7	∞	-88	F	R	
	S8	26 700	R	F	F	
	S9	13 300	R	F	F	
	S10	8 000	-67	R	+33	
	S11	4 000	-40	R	-90	.
	S12	2 675	-72	-83	R	.
	S12A	CONTROL	-42	-58	R	.
POLYESTER	S13	∞	R	F	F	
	S14	26 500	-93	F	F	.
	S15	13 750	-73	F	F	.
	S16	8 250	-93	F	-71	.
	S17	5 500	-82	F	-88	.
	S18	2 750	0	F	0	
	S18A	CONTROL	-65	F	-50	.

F = impossible to test due either

R = value too low to be recorded

B

TABLE 3 (contd.)

	Modulus at 200 per cent extension			Modulus at 300 per cent extension		
)	80°C (dry)	80°C (wet)	65°C (STF)	80°C (dry)	80°C (wet)	65°C (STF)
	-50	F	R	R	F	R
	R	F	F	R	F	F
	R	F	F	R	F	F
	-20	R	+20	-14	R	+71
	-42	-84	-89	-42	-82	-
	-60	-78	R	-	-	-
	-44	-52	R	-	-	-
	R	F	F	R	F	F
	-39	F	F	R	F	F
	-65	F	F	-53	F	F
	-80	F	-39	-78	F	- -40
	-74	F	-82	-73	F	-73
	0	F	+65	+ 2	F	L
	-50	F	-	-25	F	R

due either to swelling or disintegration

recorded or not recorded

S. No. 132/70/MS

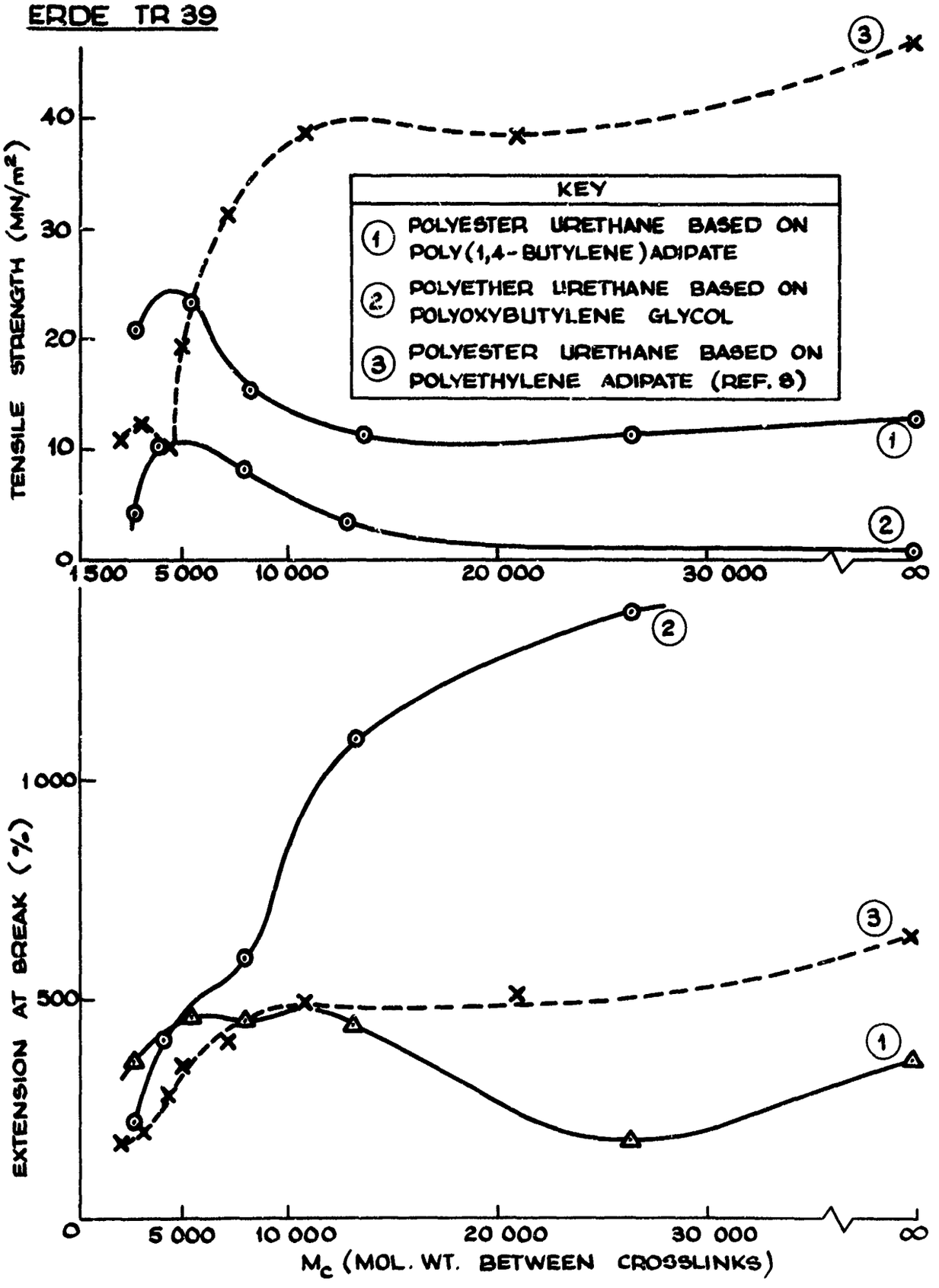

FIG.1 CHANGES IN TENSILE STRENGTH AND EXTENSION AT BREAK WITH CROSSLINK DENSITY.

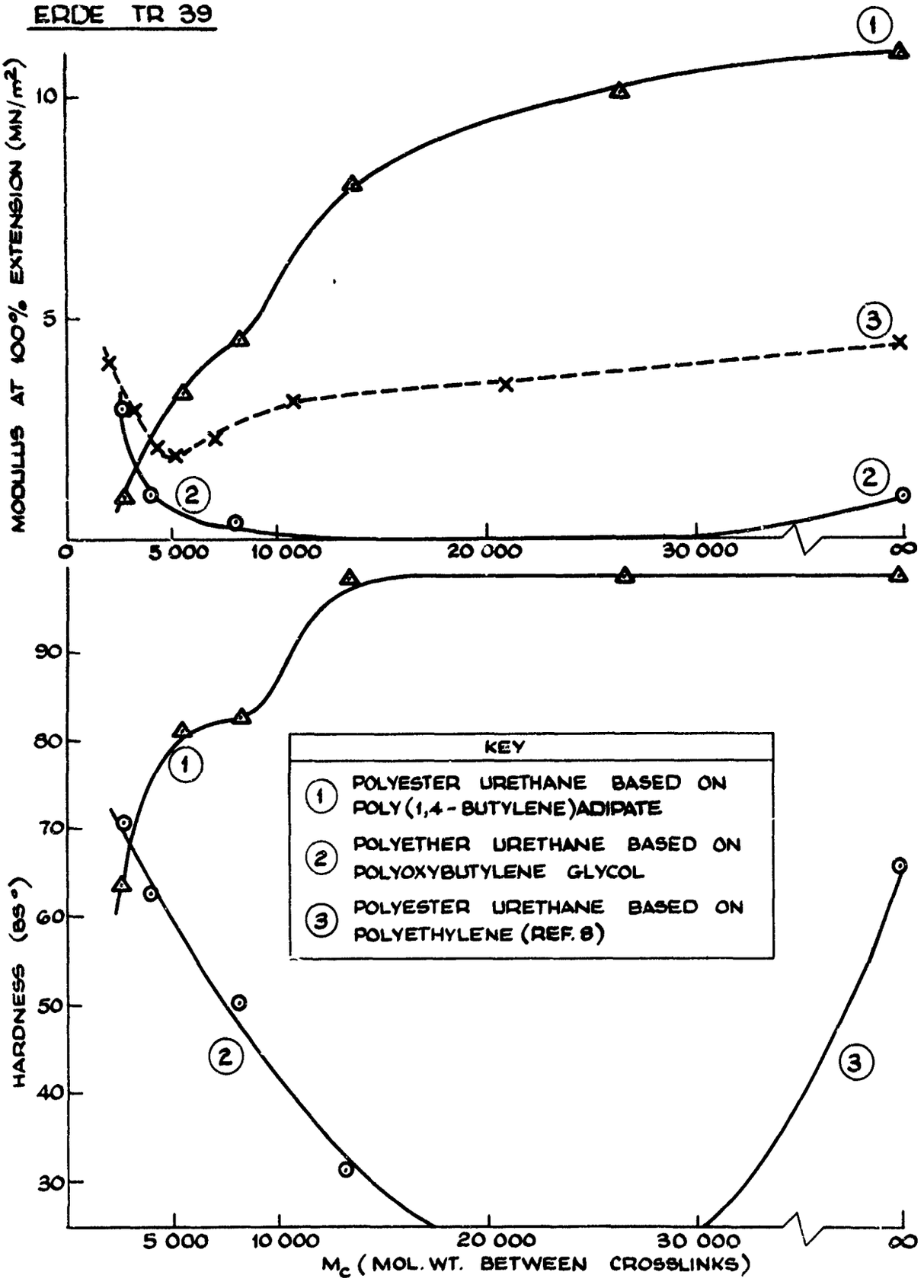

FIG. 2 CHANGES IN MODULUS (AT 100% EXTENSION) AND HARDNESS WITH CROSSLINK DENSITY.

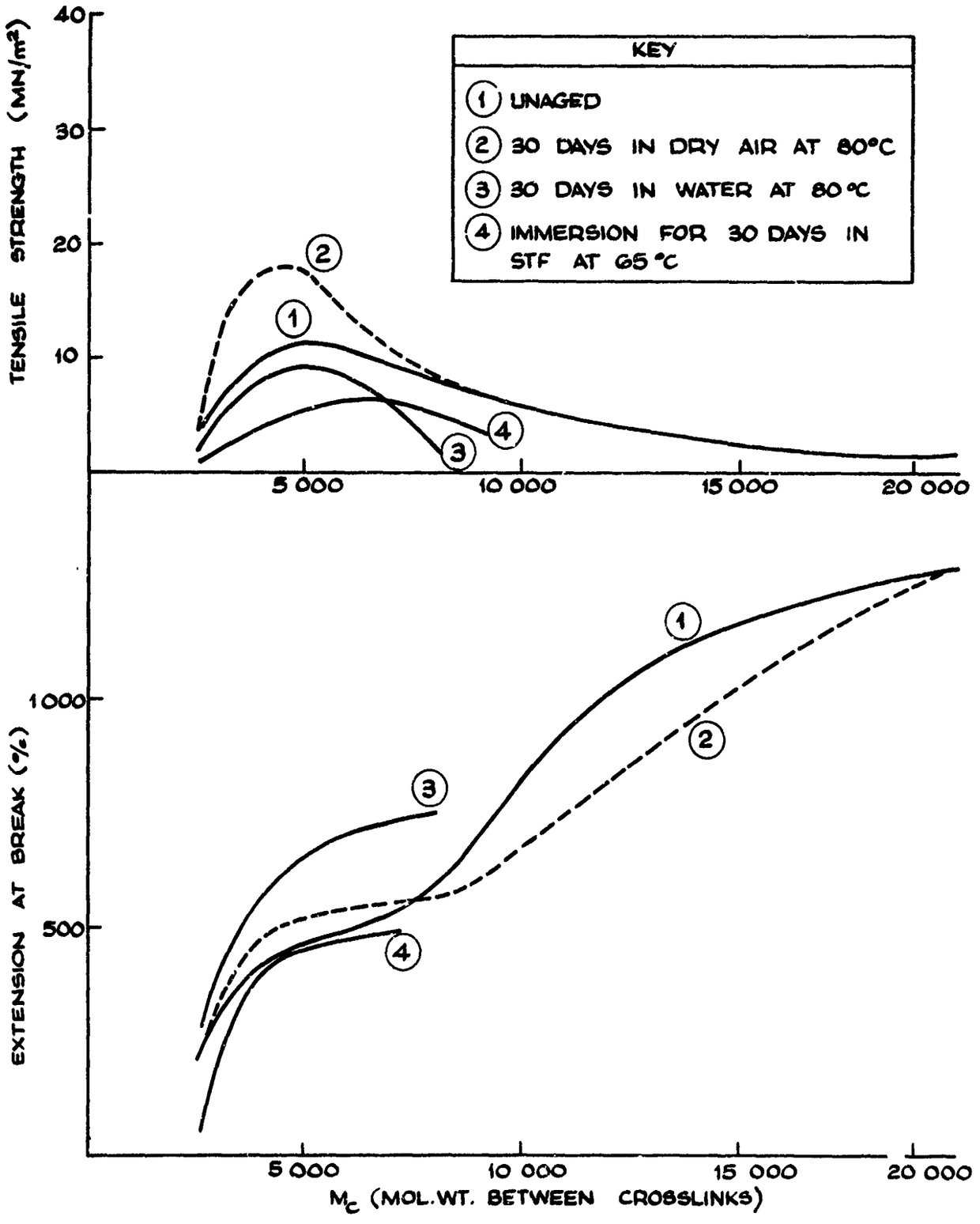

FIG.3 EFFECT OF AGEING ON PHYSICAL PROPERTIES OF POLYETHER URETHANE ELASTOMERS BASED ON POLYOXYBUTYLENE GLYCOL OF DIFFERENT DEGREES OF CROSSLINK DENSITY.

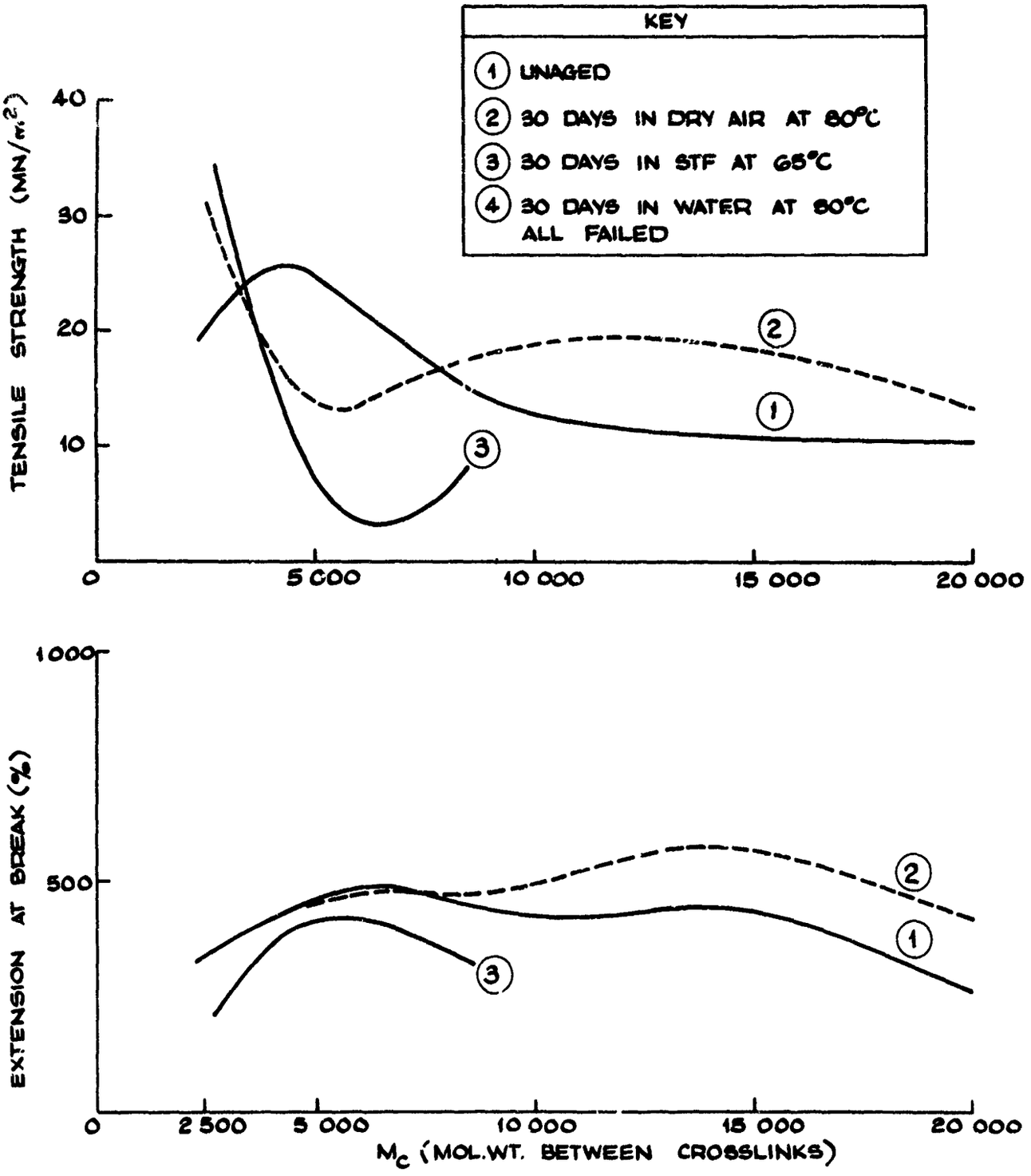

FIG.4 EFFECT OF AGEING ON PHYSICAL PROPERTIES OF POLYESTER URETHANE ELASTOMERS BASED ON POLY (1,4-BUTYLENE) ADIPATE OF DIFFERENT CROSSLINK DENSITY.